Phytochemistry, Vol. 25, No. 4, pp. 972–973, 1986.
Printed in Great Britain.

0031–9422/86 \$3.00 + 0.00

ISOLATION OF TRI-(α-METHYLENE-γ-BUTYROLACTONYL)AMINE FROM *BELLENDENA MONTANA*

I. Ralph C. Bick, John W. Gillard and Huck-Meng Leow

Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia

(*Received* 5 *September* 1985)

Key Word Index—*Bellendena montana*; Proteaceae; lactone alkaloids; tri-(α-methylene-γ-butyrolactonyl)amine.

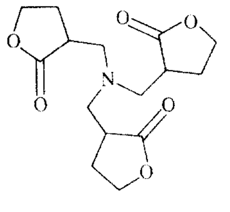
Abstract—A minor base previously reported from *Bellendena montana* has been shown to be tri-(α-methylene-γ-butyrolactonyl)amine. It appears to be a diastereomer of an artefact obtained from *Garnieria spathulaefolia*.

Among the crystalline minor bases isolated from the Tasmanian endemic plant *Bellendena montana* R.Br. (Proteaceae) [1] was a compound provisionally designated B2, mp 186–187°, $[\alpha]_D^{19}$ +80° ($CHCl_3$), that analysed for $C_{15}H_{21}NO_6$. The substance showed no resemblance in its properties to the tropane alkaloids that formed the major basic constituents of the plant: its UV spectrum indicated the presence of a feeble chromophore, presumably a γ-lactone carbonyl from the strong peaks at 1750, 1170 and 1010 cm^{-1} in the IR spectrum. The presence of at least one γ-lactone group was confirmed by absorptions around δ178 in the ^{13}C NMR spectrum, which consisted of five signals or closely related pairs of signals only. Apart from the carbonyl absorptions, the rest were all due to *sp*^{3} carbons, and three of them, around δ38, 28 and 67, could be ascribed to α, β and γ carbons respectively of γ-lactone groupings; the remaining signal pair, around δ55, corresponded to carbons attached to nitrogen. The essential simplicity of the spectrum indicated a high degree of symmetry in the molecule, and this was confirmed by a preliminary X-ray crystallographic examination, which pointed to a central nitrogen with three identical or very similar $C_5H_7O_2$ units attached to it.

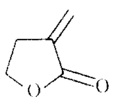
The ^{1}H NMR spectrum was difficult to analyse in detail owing to overlapping of signals, but it largely confirmed the structural pattern deduced from the X-ray and other spectroscopic evidence. Four groups of multiplet signals could be distinguished: one located between δ4.50 and 4.05, corresponding to six protons on carbons adjacent to oxygen, i.e. in the γ-methylene groups of three γ-lactone rings; another due to six protons resonating between δ2.55 and 1.90, which could be attributed to those on β-methylene carbons; a further multiplet between δ3.25 and 2.90 produced by three methine protons adjacent to the carbonyls; and the remaining signals from six protons between δ2.90 and 2.55, which could be assigned to three pairs of geminal protons adjacent to nitrogen. The evidence shows that the three methylene groups that incorporate the latter must be substituted at α-positions in the lactone rings. The resulting structure (**1**) [2] is further supported by the MS, which is characterized by a very weak molecular ion and a base peak at *m/z* 226 corresponding to loss of a $C_4H_5O_2$ lactone unit by α-cleavage; subsequent fragmentation of this ion by an onium reaction with loss of $C_5H_6O_2$ produces another intense peak at *m/z* 128.

The substance tri-(α-methylene-γ-butyrolactonyl)-amine (**1**) has recently been isolated from extracts of the proteaceous plant *Garnieria spathulaefolia* by Lounasmaa *et al.* [3], who have adduced evidence to show that it is an artefact, probably formed from α-methylene-γ-butyrolactone (**2**) and ammonia during extraction and work-up. It is unlikely that the corresponding compound isolated from *B. montana* has a similar origin since it has a considerable optical rotation, and furthermore there are small but significant differences in the ^{13}C NMR spectra for samples from the two plants: as mentioned for the material of Tasmanian origin, some of the signals appear as a pair of distinct peaks 0.2 ppm apart, in which one component has an intensity approximately double the other. These include the signals for the chiral carbons, and also those for the carbonyls and for the methylene carbons attached to nitrogen, both of which are adjacent to the chiral centres; the resonances of the remaining β- and γ-carbons, moreover, are distinctly broadened. This may be interpreted as indicating a difference in chirality at the α-carbon of one lactone residue as compared to the other two in the base isolated from *B. montana*, which would thus appear to be diastereomer of the artefact obtained from *G. spathulaefolia*.

Compound **1**, when first isolated, is readily soluble in chloroform and other organic solvents, from which it may



1



2

be crystallized; however, repeated recrystallization or prolonged standing in solution effects a change in its properties, and it becomes very sparingly soluble in most solvents. This could be due to opening of the lactone rings by hydrolysis followed by the formation of a betaine. A more rigorous examination of the compound was precluded by lack of material.

EXPERIMENTAL

The isolation of **1** has been described [1]. IR, ^{1}H NMR, ^{13}C NMR and EIMS: see text. UV $\lambda_{\max}^{\mathrm{EtOH}}$ (log ε): 207 (3.20), 275 (2.42). Found: C, 57.62; H, 6.89; N, 4.38. $C_{15}H_{21}NO_6$ requires C, 57.88; H, 6.75; N, 4.50%. The base formed a picrate, mp 209–211°.

Acknowledgements—We thank the Australian Research Grants Committee for financial support for this work. We are grateful also to Drs R. Brownlee and J. Reiss of La Trobe University for the ^{13}C NMR spectrum. The award of a Commonwealth Postgraduate Scholarship (to J.W.G.) and of a University of Tasmania Special Postgraduate Research Scholarship (to H.-M.L.) is also thankfully acknowledged.

REFERENCES

1. Bick, I. R. C., Gillard, J. W. and Leow, H.-M. (1979) *Aust. J. Chem.* **32**, 1827.
2. Leow, H.-M. (1979) Ph.D. thesis, University of Tasmania, Hobart.
3. Lounasmaa, M., Tolvanen, A., Hilturnen, L., Pusset, J. and Chauvière, G. (1985) *Heterocycles* **23**, 939.

Phytochemistry, Vol. 25, No. 4, pp. 973–975, 1986.
Printed in Great Britain.
0031–9422/86 $3.00 + 0.00

THE C_{19}-DITERPENOID ALKALOIDS OF *ACONITUM DELPHINIFOLIUM*

V. Nambi Aiyar, Palaniappan Kulanthaivel and Michael Benn
Chemistry Department, The University, Calgary, Alberta, Canada, T2N 1N4

(*Received* 24 *September* 1985)

Key Word Index—*Aconitum delphinifolium*; Ranunculaceae; diterpenoid alkaloids; 14-*O*-acetylsachaconitine.

Abstract—Nine C_{19}-diterpenoid alkaloids were isolated from *Aconitum delphinifolium*, one of which was the apparently previously unknown 14-*O*-acetylsachaconitine.

INTRODUCTION

One of the few aconites native to N. America, *Aconitum delphinifolium* DC., has a range that extends from the Aleutian islands and Alaska down through the mountains of W. Canada into British Columbia and Alberta [1]. In all these places the plant has the reputation of being toxic, and it has been reported to have been used as an ingredient in an arrow-poison used by the aboriginal inhabitants of the Pacific North-West [2]. Such toxic properties appeared to us to be most likely due to the diterpenoid alkaloids to be expected in an aconite [3] and we therefore undertook an investigation of the alkaloids present in Albertan communities of *A. delphinifolium*.

RESULTS AND DISCUSSION

Whole plants were collected while in blossom and divided into flowers, leaves and stems, and roots. These all proved to contain substantial amounts of alkaloids, the flowers being particularly rich, but there seemed to be no qualitative differences in the distribution of individual components within the plant parts. Fractionation of the mixed alkaloids by conventional chromatographic procedures resulted in the isolation of nine C_{19}-diterpenoids. Analyses of the IR, mass, ^{1}H and ^{13}C NMR spectra of these compounds resulted in the identification of eight of these as known alkaloids: 14-*O*-acetylbrowniine (**1**), 14-*O*-acetyltalatisamine (**2**), browniine (**3**), condelphine (**4**), delcosine (**5**), delphinifoline (**6**), isotalatizidine (**7**) and virescenine (**8**) [4]. The ninth was similarly deduced to be 14-*O*-acetylsachaconitine (**9**), a compound which, so far as we have been able to ascertain, has not been described before. Thus MS suggested a $C_{25}H_{39}NO_5$ molecular formula; IR spectroscopy revealed the presence of hydroxyl and ester functionalities; and the ^{1}H NMR spectrum contained absorptions due to a quaternary *C*-methyl, an *N*-ethyl, an *O*-acetyl, two methoxy groups and, as well, one expected for H-14 of a lycoctonine-skeleton acyloxylated in this position [4]. The ^{13}C NMR data (see Table 1) was consistent with this information, and the